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J. F. Cooper, N. Cherepy, G. Berry, A. Pasternak, T. Surles, M. Steinberg

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DIRECT CARBON CONVERSION: APPLICATION TO THE EFFICIENT CONVERSION OF FOSSIL FUELS TO ELECTRICITY

John F. Cooper,[1]* Nerine Cherepy,* Gene Berry, Alan Pasternak, and Terry Surles
Lawrence Livermore National Laboratory, Livermore CA 94550
Meyer Steinberg
Brookhaven National Laboratory, Upton NY 11973

ABSTRACT

We introduce a concept for efficient conversion of fossil fuels to electricity that entails the decomposition of fossil-derived hydrocarbons into carbon and hydrogen, and electrochemical conversion of these fuels in separate fuel cells. Carbon/air fuel cells have the advantages of near zero entropy change and associated heat production (allowing 100% theoretical conversion efficiency). The activities of the C fuel and CO_2 product are invariant, allowing constant EMF and full utilization of fuel in single pass mode of operation. System efficiency estimates were conducted for several routes involving sequential extraction of a hydrocarbon from the fossil resource by (hydro) pyrolysis followed by thermal decomposition. The total energy conversion efficiencies of the processes were estimated to be (1) 80% for direct conversion of petroleum coke; (2) 67% HHV for CH_4; (3) 72% HHV for heavy oil (modeled using properties of decane); (4) 75.5% HHV (83% LHV) for natural gas conversion with a Rankine bottoming cycle for the H_2 portion; and (5) 69% HHV for conversion of low rank coals and lignite through hydrogenation and pyrolysis of the CH_4 intermediate. The cost of carbon fuel is roughly $7/GJ, based on the cost of the pyrolysis step in the industrial furnace black process. Cell hardware costs are estimated to be less than $500/kW.

INTRODUCTION

Concerns over global warming have motivated the search for more efficient technologies for electric power generation from fossil fuels. Today, 90% of electric power is produced from coal, petroleum or natural gas. In addition to reducing the carbon dioxide emissions per unit of electric power, exercising an option of deep geologic or ocean sequestration for the CO_2 would reduce emissions further and possibly help curtail global warming [1,2].

As a means of reducing greenhouse-gas emissions, we introduce an innovative concept for conversion of fossil fuel resources into electricity at efficiencies of 67-80% (based on the standard heat of oxidation of the primary fuel, ΔH^0_{298}) [3-5]. This concept entails the following sequence: (1) extraction of hydrocarbons from fossil fuels; (2) thermal decomposition into elemental carbon and hydrogen, and (3) electrochemical conversion of the carbon and hydrogen in (separate) fuel cells. The overall process is depicted in Figure 1.

Central to this concept is direct carbon conversion—a process that is similar to a fuel cell but differs in that carbon, not hydrogen, is the fuel. The cell sustains the reaction,

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[1] Corresponding author. * Active Electrochemical Society Member

$C + O_2 = CO_2$ (E ~ 1.0 V, T = 700-850 °C). The fuel is in the form of fine particulates (~100 nm) distributed by entrainment in a flow of CO_2 to the cells to form a slurry of carbon in the melt. The byproduct stream of CO_2 is pure. This affords the option for sequestration without additional collection and separation costs. Alternatively, the CO_2 can be used in enhanced oil or gas recovery. Our experimental program tested carbon materials with orders of magnitude spreads in anode reactivity measured as cell power density. One class of materials yields energy at up to about 1kW/m^2—sufficiently high to make practical the use of the cell in electric utility applications.

The carbons used in such cells are highly disordered on the nanometer scale, relative to graphite. Such disordered or "turbostratic" carbons can be produced by controlled pyrolysis (thermal decomposition) of hydrocarbons extracted from coal, petroleum or natural gas. For coal and lignite, hydrocarbons may be produced by hydrogenation (hydropyrolysis), with the recycle of the hydrogen reagent following pyrolysis. Starting with methane feedstock for carbon black manufacture, the ash entrained into the carbon (<0.03%) does not jeopardize cell life or economics. Electrochemical and systems aspects have been reported concurrently [3,4]. The full report of the current study is published as a laboratory report [5].

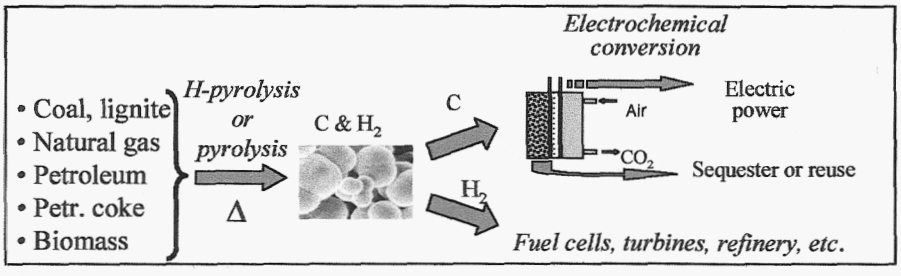

Fig. 1. We are investigating the sequence for electric power generation: (1) extraction of CH_x, (2) pyrolysis to C and H_2, and (3) conversion in separate fuel cells. The pure CO_2 product may be sequestered or reused in enhanced oil or gas recovery.

BACKGROUND

Attempts to derive electricity "direct from coal" date from the 19th Century. William Jacques operated cells using sintered coke electrodes in an alkaline electrolyte (NaOH), which yield Na_2CO_3 as a product. Since the molten NaOH electrolyte was exhausted by the reaction, the cell could not operate as a fuel cell. Nonetheless very high current densities were exhibited (1 kW/m^2). The C/O_2 reaction in various electrolytes was investigated intermittently in the 20th Century, as reviewed by Liebhafsky and Cairns [6], without practical implementation. Weaver [7,8] operated cells using various forms of devolatilized coal, which have a turbostratic disorder and are hence quite reactive. Weaver showed polarizations as low as 0.2 V (from theoretical) at rates of 1 kA/m^2. Entrainment of coal ash gradually fouled the electrolyte, and the configurations tested required fabrication and distribution of rigid electrodes with fixed current collectors. Weaver showed that carbon dissolution occurred with four electrons transferred per mole, at temperatures as high as 750 °C. Vutetakis and Skidmore investigated a number of half-cells using slurries of granular carbon materials and a gold current collector immersed in the electrolyte, finding carbon structure to be important in anode polarization. While the carbon dissolution occurred with a net transfer of 4 electrons per mole, Boudouard corrosion of carbon still occurred within the bulk slurry, according to $C + CO_2 = 2\ CO$. [9,10]

Hemmes and coworkers (Delft University of Technology, The Netherlands) are examining alternative systems for partial electrochemical carbon conversion [11-15]. In one approach, the carbon (or coke) is electrochemically oxidized only half way, to CO, and a very high cell voltage (relative to heat of reaction) is achieved because of the substantial entropy increase of the reaction. The byproduct CO is then consumed in a turbine or used for its heating value in other processes. This approach is supported by earlier work by Nakagawa and Ishida [16], who conducted an exergy model on the conversion of elemental carbon in a gas-phase solid oxide fuel cell. Here the CO was regenerated from the CO_2 product by reaction with the carbon (the Boudouard reaction). Gur and Huggins [17] also experimented with partial oxidation of elemental carbon, using oxide ion transport across a thin zirconia membrane. They demonstrated high efficiencies at low rates, and suggested that turbostratic carbons might be discharged at practical rates.

In summary, previous efforts to develop practical C/O_2 fuel cells were hindered by entrainment of ash with the fuel carbon, which exhausted the electrolyte; by impractically low anode reaction rates; and by the costs and difficulties of electrode manufacture and the distribution to the cells.

DIRECT CARBON CONVERSION

The direct carbon conversion cell uses a slurry of carbon particles in a molten salt. Carbon black particles (typically, 30-100 nm size) are distributed by entrainment in a CO_2 carrier gas into one chamber of the electrochemical cell. (Fig. 2). The CO_2 product gas is evolved from the anode chamber. Some CO_2 diffuses across the thin separator to react with atmospheric oxygen to balance the cathodic reaction. Solid oxide analogues are also candidates.

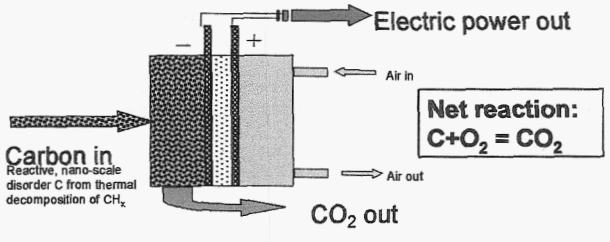

Fig.2. A direct carbon conversion cell, or carbon fuel cell, reacts particulate carbon with atmospheric oxygen in a cell with a molten salt electrolyte at 750-850 °C

The electrode and cell net reactions are:

$C + 2\ CO_3^{2-} = 3CO_2 + 4\ e^-$	Anode
$O_2 + 2CO_2 + 4\ e^- = 2CO_3^{2-}$	Cathode
$C + O_2 = CO_2$	$E° = 1.02$ V at T= 800 °C

Cell polarization is dominated by the anode reaction. The electrode polarization can vary by over an order of magnitude depending on crystallographic disorder of the carbon material. While the polarization is far greater than that of the hydrogen fuel cell (which may show peak power densities exceeding 1 W/cm^2), the cell voltage of 0.8 V at 1 kW/m^2 is sufficient for many fuel cell or fuel battery applications. Since these turbostratic carbons are synthesized from the pyrolysis of otherwise pure hydrocarbons,

ash entrainment into the cells is avoided. The anode exists as a fine suspension of carbon particles in the melt, which might be recharged by entrainment of the particles into the cell using a CO_2 carrier stream.

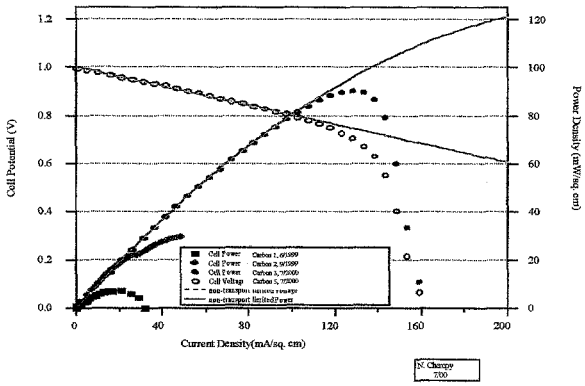

Fig. 3a. Polarization and power curves for three different samples of carbon produced by pyrolysis. These carbons are produced by the same fundamental process (thermal or oxidative decomposition) and differ only in the degree and nature of disorder on the nanoscale.

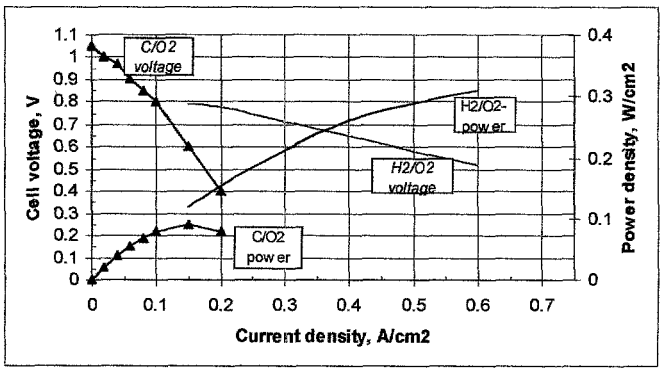

Fig. 3b. Specific power achieved by C/air cells is not greatly lower than that achieved by the Westinghouse SOFC technology (3 ATM; 85% utilization, [18]), when the comparison is made at the voltage of intended operation (0.8 V, ~ 80% voltage efficiency.

THERMODYNAMIC BASIS

The value of carbon (relative to hydrogen) as an electrochemical fuel derives from thermodynamic aspects of the C/O_2 reaction. First, the entropy change of the C/O_2 reaction is essentially zero, allowing theoretical efficiencies ($\Delta G(T)/\Delta H_{298}$) of 100 % (cf. H_2/O_2 theoretical efficiency of 70%). Second, the thermodynamic activity of the carbon fuel and the CO_2 product are spatially and temporally invariant, and the EMF is therefore constant. This allows 100% utilization of the carbon fuel in single pass (cf. hydrogen utilizations of 75-85%). The product efficiencies for C/O_2 are roughly 80% for cell operation. Any hydrocarbon oil or gas (represented by CH_x) can be decomposed into a turbostratic carbon and hydrogen—a process that consumes a small fraction (3-9%) of the heat of combustion of the hydrocarbon. In summary, what gives this route its fundamental advantages in energy conversion is that it derives the greatest possible fraction of energy from the fossil resource using an electrochemical reaction ($C+O_2 = CO_2$) that is comparatively simple to operate at efficiencies above 80%, requiring neither explicit capture and recycle of heat associated with entropy reduction nor bottoming cycles to consume unreacted fuel.

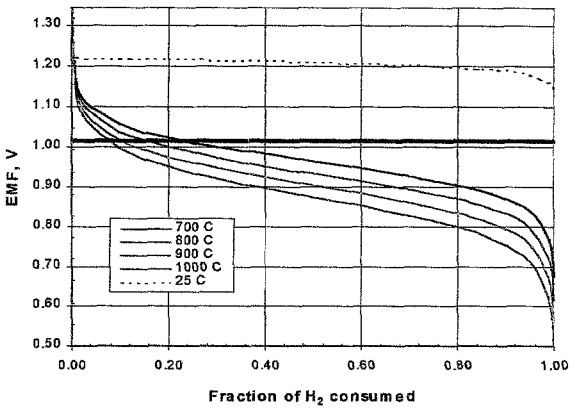

Fig 4. The driving force for electrochemical power generation, or EMF, depends on extent of reaction and position in the cell for high-temperature H_2/O_2 cells, but is invariant for C cells (T = 700-900 °C, solid horizontal line) and a low temperature PEM fuel cells (broken line). This allows full utilization of the carbon fuel. [See ref [6]].

The electrochemical efficiencies of various fuel cells are compared in Table 1, as the product of three terms, denoting theoretical efficiency, fuel utilization μ and voltage efficiency, respectively. (This discussion follows that in general fuel cell references [6, 18, 19]).

$$Net\ efficiency = (\Delta G_T/\Delta H_{298}) \times (\mu) \times (V(i)/E^\circ)$$

Table 1. Comparison of efficiencies of fuel cells using synthetic or refined fuels. Operating temperature = 750 °C. Energy cost of fuel synthesis is excluded.

Fuel	$\Delta G/\Delta H^\circ_{298}$	Fuel utilization factor	Voltage efficiency, $V(i)/E^\circ$	Net efficiency
C	1.003	1.0	0.8	0.80
H_2	0.70	0.75-0.85	0.8	0.42-0.48
CH_4[a]	0.89	0.75-0.85	0.8	0.53-0.60

[a]Assumes efficient internal steam reforming reaction. Direct electrochemical discharge of methane at a catalyzed surface does not occur at practical rates.

STRUCTURE AND PURITY REQUIREMENTS OF CARBON FUELS

The materials requirements placed on carbon fuels derive primarily from factors of crystallographic structure (measured on the <100 nm scale) and to a lesser extent from specific surface area of the particles. The relation of structure, form and surface area to reactivity in oxidation is reviewed by Kinoshita [20], and the relation of structure to pyrolysis conditions is reviewed by Donnet [21].

The identity of the most reactive carbon materials is, as yet, proprietary. However, the industrial products closest to our requirements for fuels are the furnace and thermal blacks made from the following feedstock materials: methane, steam cracker oils and cat cracker oils, and coal-tar distillates. Principal metal impurities in petroleum-derived cokes are nickel and vanadium. Most carbon blacks contain a residual ash (from cat crackers or pyrolysis vessel degradation) of about 0.02-0.05 %. This should have no effect on system performance, cost or life, as the rate of accumulation would be very slow compared with the throughput of carbon.

In all, the products of conventional furnace or thermal black processes are adequate in purity for use in direct conversion cells, and form a basis for the estimates of

costs and process efficiencies. Table 2 lists approximate ash and sulfur contained in common feedstock materials used for making carbon blacks.

Table 2. Impurities in feedstock materials used in carbon black manufacture [21].

Feedstock	ash, %	S, %
Methane derived from NG	--	--
Steam cracker products: naphtha, gas oil	0.02	0.2
Cat cracker products: heavy petroleum fraction	0.05	2.1
Coal tar distillates	0.04	0.6

ESTIMATES OF CONVERSION EFFICIENCY: FOSSIL FUELS TO ELECTRICITY

System efficiency estimates were conducted for several routes involving sequential (1) extraction of a hydrocarbon from the fossil resource by (hydro) pyrolysis, (2) thermal decomposition to a reactive carbon, followed by (3) conversion of the carbon and byproduct hydrogen in (separate) fuel cells.

The total energy efficiencies of the process were estimated to be (1) 80% for direct conversion of petroleum coke byproducts of oil refining; (2) 67% HHV for pyrolysis of CH_4; (3) 72% HHV for pyrolysis of heavy oil (modeled using properties of decane); (4) 75.5% HHV (83% LHV) for natural gas conversion with a Rankine bottoming cycle for the H_2 portion; and (5) 69% HHV for conversion of low rank coals and lignite through hydrogenation of the solid fuel and pyrolysis of the methane intermediate. These approaches are summarized in Table 5. Details of these calculations can be found in the full report. [5] All systems exceed the efficiency goal corresponding to 70% LHV, which has been set for the "21st century Fuel Cell." [22]

Petroleum Cokes

The first entry in Table 5 describes perhaps the simplest route to carbon conversion, starting with the petroleum coke as a byproduct from oil refining. This product represents 2-10% of petroleum crude. Part of this material is used as the anode fuel in the Hall process for making aluminum. Petroleum coke has both sulfur and ash components. If the coking process is adjusted to limit ash to < 0.1 %, entrainment of ash into the cell has no negative effect on system economics or cell life. The sulfur is rejected as COS, which can be decomposed by hydrolysis into CO_2 and H_2S. The presence of sulfur requires that metal parts in the anode be replaced by conductive graphite, which is 1000-fold less reactive than turbostratic carbons under consideration. The coke reactivity needs to be maximized by limiting graphitization of green cokes.

Natural Gas, Pyrolysis and Fuel Cells Alone.

Entry 2 of Table 5 is a baseline process for conversion of natural gas. The methane component is pyrolyzed using as heat the unconsumed fraction of the hydrogen gas exhausted from the fuel cell operating at a utilization of 80%. This provides a high fuel cell voltage and the 20% unconsumed hydrogen provides sufficient heat to drive the pyrolysis process at 80% thermal efficiency (0.2x58.7 kcal/mole x 2 mole = 24 kcal). Enthalpy of the exhaust gas streams is recovered and used to preheat the fuels. The

overall efficiency is high (67% HHV) and the process is simple, not requiring turbo charging or bottoming cycles.

Petroleum Vacuum Gas Oil

This approach is perhaps the most straightforward extrapolation from current practice, as fuel oils normally used in carbon black production easily meet requirements for low ash and afford excellent control over the nanostructure of the product. Intermediate cracking fractions are common feedstock materials for furnace black production. We have modeled the energy balance here using tabulated data for decane. The heat of pyrolysis is less than 4% of the fuel value. The hydrogen stream is used at 90% single pass efficiency in a fuel cell, with recovery of unconsumed hydrogen by condensation of steam. Enthalpy of the exhaust gas streams is recovered and used to preheat the fuels. The overall efficiency is about 74% HHV (77% LHV)—the highest we have seen proposed for a simple system without bottoming cycles.

Natural Gas, Pyrolysis, Fuel Cells and Rankine Cycle.

One of us (Steinberg) analyzed the generic system shown in Table 5 entry 4, which decomposes methane using natural gas thermal energy and entrains the carbon product directly into a molten salt in proximity to the cell. Hot exhausts are combined to boil water for a Rankine cycle generator. The assumptions of efficiencies associated with each component are given in Table 3.

The net efficiency of the system is the ratio of the electric power outputs to the sum of the thermal values (HHV) of all fuel inputs. This efficiency is then given by:

Efficiency = (85+76+27)/(213+23+13) = 75.5% HHV (83.4% LHV)

This is significantly more efficient than the simple pyrolysis process of Table 5 entry2, but requires an increase in complexity to recover waste heat and hydrogen fuel for use in steam bottoming cycle.

Table 3. Methane, fuel cell and boiler: component operating conditions and efficiencies.

Unit	Pressure Atm	Temperature, °C	Efficiency, %
CH_4 decomposer	1-5	800-1000	80
C/air cell	1-5	750-1000	86.3
SOFC	1-5	1000	55.6 (90% utilization)
Boiler, Rankine cycle	70	600	38

Hydropyrolysis, Fuel Cell and Rankine Cycle

Steinberg also analyzed a system for conversion of brown coal to methane, followed by pyrolysis and recycle of the hydrogen. Process summary operating conditions and efficiencies are given in Table 4.

The overall reaction used in the computation is for lignite:

$$CH_{0.8}O_{0.22} = C + 0.18\ H_2 + 0.22\ H_2O$$

The net efficiency is the ratio of the electric power output (84.6 + 7.5 +5.9 kcal-e) to the thermal value of the inputs (1.27*113 kcal). This indicates a net efficiency of 69% HHV (76% LHV). This is the most efficient process yet proposed for coal.

Table 4. Parameters for the operation of a hydropyrolysis conversion of low-rank coal.

Unit	Pressure, Atm.	Temperature, °C	Efficiency
Hydropyrolyzer, fluidized bed	70	800-900	80
Methane decomposition to thermal black	1-5	900-1000	80
Carbon cell 84.6 kcal-e	1-5	750-1000	86.3
SOFC 7.5 kcal-e	5	1000	55.6
Boiler, Rankine Cycle: 5.9 kcal-e	70	600	38

ESTIMATES OF FUEL AND CELL COSTS AND POTENTIAL IMPACT

The costs of the processes are estimated from the costs of industrial production of carbon blacks from the feedstock of methane and various petroleum cracking fractions. Carbon blacks are produced by a long sequence of unit processes, the first of which is thermal decomposition. The cost of this first step, which determines fully the nanostructure and reactivity of the carbon fuel, is 9-11 cents/lb ($7/GJ based on combustion energy). (Subsequent stages of quenching, separations, chemical treatments, bagging, etc., are not needed in the proposed combined pyrolysis and electric power plants). Electrode grade petroleum cokes cost in the range of 1-6 $/GJ. Steam-reformed hydrogen, by comparison, was about $7/GJ. For comparison, the cost of electricity at $0.1/kWh is $27/GJ. Thus current costs of potential carbon fuels are small compared with the cost of delivered electric power. [These estimates were made prior to rapid increase in natural gas prices in mid 2000.]

The cost of the cell can be estimated from the current design of laboratory cells. Using a planar configuration with nickel felt air electrode, zirconia fabric separator saturated with melt, nickel felt anode current collector and graphite and stainless steel construction, the cost of the cell is estimated to be below $500/kW, including reasonable costs of assembly, G&A and profit markup.

The reduction achieved by implementation of such technologies on carbon dioxide emissions is inversely proportional to the increase in efficiency (a factor of 1.8-2). The marginal decrease in CO_2 emissions is 50% relative to current technologies. If the option for sequestration is exercised for the CO_2 byproduct of the cell, then CO_2 emissions are decreased by roughly a factor of 10.

The control of greenhouse emissions is a complex problem that may benefit from action on multiple fronts: conservation, reduction of non-industrial burning, electrification or CNG for transportation, non-fossil electricity production (renewable and nuclear) and shift in industrial thermal energy and residential space heating to high-hydrogen fuels—e.g., natural gas. Nevertheless, we believe there is significant value in development of a technology that doubles the yield of electric energy from each unit of fossil resource. The solution to the global problem is beyond the scope of power production technology alone.

CONCLUSIONS

The conclusions of our study [5] are as follows.

1. *Need for high efficiency conversion processes.* The curtailment of carbon dioxide emissions from fossil fuel combustion would benefit from technology for electric power production having efficiencies well beyond the levels achieved in conventional utilities (35-40%), fuel or combined cycle plants (45-55%, HHV).
2. *Carbon conversion.* Elemental carbon, derived from hydrocarbons by controlled pyrolysis, can be converted to electricity at efficiencies of 80% at rates practical for utility application. The byproduct CO_2 is suitable for sequestration or reuse without additional collection and purifications costs. The rate of the cell discharge depends on nanometer scale structure of carbon.
3. *Thermodynamic basis for efficiency of direct carbon conversion.* Direct carbon conversion has efficiency advantages as an electrochemical fuel. The theoretical efficiency ($\Delta G_T/\Delta H_{std}$) is 100.3%. The carbon reactant and CO_2 product exist at unit activity in separate phases. This produces an invariant EMF and allows full utilization in single pass mode of operation.
4. *Reactant feed and properties.* Pneumatic distribution of carbon is proposed. At 1 kA/m^2, the rate of carbon transport is 113 g/m^2-h.
5. *Systems for conversion of fossil fuels to reactive carbons and hydrogen.* Electrode grades petroleum coke is produced as a byproduct of petroleum refining. Five routes connecting petroleum coke, refinery products, natural gas and low rank coals were proposed with efficiencies above 67% HHV.
6. *Costs of cell and turbostratic carbons.* Based on current cell hardware, using graphite and zirconia fabric construction, cell cost estimates are about $500/kW. Turbostratic carbons are produced in pyrolysis units, yielding product with reactivity depending on operating conditions and fuel mixes. However, the cost of pyrolysis (regardless of nanostructure) is bound: 9-11 cents per pound, corresponding to about $7/GJ.
7. *Critical tasks in the development of Direct Carbon Conversion as an option for efficient power production.* Critical steps in the development of the technology for fossil energy conversion through direct carbon fuel cells include: (1) Extended duration tests of the cell on an engineering scale (1 kW) using pneumatic feed of carbons. (2) Development of a predictive theory relating carbon electrochemical and chemical activity to measurable parameters of structure, and relating this structure to the conditions of pyrolysis. (3) Studies of conversion of high-sulfur petroleum cokes and coal tars. (4) Detailed examination of alternative means of extraction of hydrocarbons from coal and lignite by pyrolysis, hydro-pyrolysis or solvent extraction.

Table 5. Systems Considered in the Evaluation

No.	System diagram	Assumptions and requirements	Efficiency
1.	Electrode-grade petroleum coke ($1/GJ @$30/ton) → Air, CO_2	1. Electrode grade petroleum, with minor alterations in thermal treatment of green coke; ash < 0.3% 2. Cell voltage = 0.8 V 3. Full utilization of C electrode	80% ΔH_{std}
2.	Methane ΔH_{std} = -212.8 kcal/mol ($3.50/GJ); pyrolysis; $CH_4 = C + 2H_2$, ΔH = 18 kcal/mol; C; $2H_2$; 20% H_2 (unutilized); Air; CO_2; Air	1. Fuel cells operated at 0.86 V 2. Pyrolysis heat provided by burning unconsumed H_2 from fuel cell operating at 80% utilization 3. Pyrolysis efficiency 80% (q = 18 kcal/0.8). 4. Heat recovered from exiting gas for preheat of fuels.	67% HHV (73% LHV)
3.	$C_{10}H_{22}$ → Pyrolysis; 59.67 kcal/mol; 1 mol; 1632.35 kcal/mol HHV (1516.6 kcal/mol LHV); 10 C → Direct Carbon Conversion → 784.2 kcal-e, CO_2; 11 H_2 → Fuel cell → 431.3 kcal-e; 1 H_2; 1 H_2 → Condenser → H_2O_{liq}; E = 0.85 V; η_u = 1.0	1. Pyrolysis of a heavy oil (simulated for calculations as decane; ΔH = 60 kcal/mol; low ash, < 0.1% 2. Operation of fuel cells at 850 °C 3. Recovery of H_2 by condensation of steam 4. Full C utilization; 90% H_2 utilization, single pass, 90%. 5. Heat of CO_2 and H_2O exhaust recovered for preheat of fuels	72% HHV (77% LHV)
4.	Flue; High-T Fuel Cell; NG; CH_4 Decomposer; air; Boiler; turbine; NG; Carbon Conversion; Molten salt C-entrained; air	1. NG pyrolysis using NG, on molten salt substrate 2. High temperature fuel cells 3. Rankine steam cycle	75.5% HHV (83.4 % LHV)
5.	H_2; Slip H_2; High-T Fuel Cell; coal; Hydro-pyrolyzer; CH_4 Decomposer; air; Boiler; turbine; Carbon Conversion; air	1. Hydropyrolysis of low rank coals; slip stream of H2 converted in fuel cell. 2. High temperature fuel cells.	69% HHV (76% LHV)

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